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THE DEVELOPMENT OF A MINI PLANT CHLORINATOR FOR THE OXIDATION OF FERROUS CHLORIDE SOLUTIONS

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THE DEVELOPMENT OF A MINI PLANT CHLORINATOR FOR THE OXIDATION OF FERROUS CHLORIDE SOLUTIONS

by

K.G. Tan* and P.L. Bedard**

ABSTRACT

A continuous reactor for the oxidation of ferrous chloride leach solutions with chlorine was constructed and tested. The design target the virtually complete chlorination of up to 1 L/min flows of raffinate containing about 1 M $FeCl_2$, 3 M NaCl, 0.5 M HCl and minor amounts of $PbCl_2$, $ZnCl_2$ and $CaSO_4$.

A cocurrent packed glass column 1.2 m high and 5 cm diameter was selected, and the reactor was packed to a height of 50 cm with 1 cm diameter glass Raschig rings. Better operational control was achieved by scrubbing the exit gas from the column with fresh ferrous chloride solution in a 2-L capacity agitated precontactor. The apparatus performed well up to the limits of the available accessories (pumps, rotameters, etc.), and the extent of chlorination was conveniently monitored by e.m.f. measurements. Solution flow rates up to 800 mL/min were achieved. Optimum conditions were 10% excess chlorine, $\geq$97% ferrous conversion and redox potentials $\geq$550 mV SCE in the exit solution.

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MISE AU POINT D'UN MINI-CHLORATEUR POUR L'OXYDATION DES SOLUTIONS DE CHLORURE FERREUX

par

K.G. Tan* et P.L. Bédard**

RÉSUMÉ

On a construit et testé un réacteur en continu pour procéder à l'oxydation de solutions de lessivage de chlorure ferreux avec du chlore. Le but de ce projet était de parvenir à la chloruration complète d'un raffinat dont le débit pouvait atteindre 1 L/min et contenait environ 1 M $FeCl_2$; 3 M NaCl; 0,5 M HCl ainsi que des quantités traces de $PbCl_2$, $ZnCl_2$ et de $CaSO_4$.

Une colonne garnie parallèle en verre mesurant 1,2 m de haut et 5 cm de diamètre a été choisie et on a ensuite garni le réacteur jusqu'à une hauteur de 50 cm avec des anneaux de Raschig de 1 cm de diamètre en verre. Un meilleur contrôle opérationnel a été atteint par l'épuration des gaz de sortie de la colonne avec une solution fraîche de chlorure ferreux dans un précontacteur agité d'une capacité de 2 L. L'appareil a bien fonctionné jusqu'aux limites que les accessoires disponibles (pompes, rotamètres, etc.) pouvaient atteindre et le degré de chloruration a été contrôlé sans inconvénient en mesurant la force électromotrice. On a réussi à produire un débit de la solution pouvant atteindre 800 mL/min. Les conditions optimales étaient de 10 % exécédent de chlore, de $\geq$97 % de conversion ferreuse et un potentiel redox de $\geq$550 mV à l'électrode au calomel dans la solution de sortie.

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INTRODUCTION

Ferric chloride leach processes, such as the one developed by the U.S. Bureau of Mines for the hydrometallurgical recovery of lead (1), are also attractive for the treatment of complex sulphide concentrates (2). Potential advantages include the absence of SO_2 emissions, good leach kinetics and selectivity, reasonable energy and reagent requirements, and byproduct recoveries. These potential advantages are to be demonstrated by an integrated mini plant campaign run on pyritic bulk concentrate and according to a modified flowsheet developed at CANMET (3).

The purpose of the present work was to address the chlorination step whereby the spent ferrous chloride leach solution (raffinate) is regenerated, totally or in part, by oxidation with chlorine. At the U.S. Bureau of Mines (1), such a leach solution was processed in a 30 cm diameter by 3 m high countercurrent contacting tower operated in a semi-batch mode to treat $\sim$20 L/min of solution at 75°C with a recirculation rate of about 21 L/min (based on fresh solution only). Although excellent chlorine utilization efficiencies of >98% were reported, the design must be improved to allow continuous chlorination in a compact mini plant scale reactor.

A comprehensive literature review of the $FeCl_2 + Cl_2$ reaction was undertaken for design purposes and the following considerations were taken into account. With the expected raffinate composition (4) of 1 M $FeCl_2$, 3 M NaCl, 8 g/L $PbCl_2$, 5 g/L $ZnCl_2$ and 5 g/L $CaSO_4$ at a pH of less than 1, the primary iron species would be aqueous chloro complexes (5,6). The complexing ability of the chloride anion can assist in the oxidation of iron (5,6) in various ways. By stabilizing the ferric product, reverse reactions are inhibited. Also the energetics of formation of an activated complex and/or the electron transfer mechanism can be improved by

favourable electronic splitting diagrams, inner and outer complex formation, opposite ion effects, or activation of the oxidant. Possible active oxidizing species are (7-9): Cl_3^- (or Cl_2), Cl_2^- (or Cl radicals) and an iron(IV) intermediate. Hypochlorite (ClO^-) is formed only at higher pHs (7). Crabtree and Schaefer (9) found a second order chlorination rate constant of about 100 L/mol.s at 30°C, in good agreement with values reported by Conocchioli et al. (8) for similarly dilute solutions at 25°C.

For heterogeneous gas-liquid reactions, a wide variety of contactors are available, including stirred tank reactors and packed columns (10-12). Levenspiel (10) suggests that the process is gas film controlled for highly soluble gases and very fast reactions, and he recommends the use of packed columns because of their flexibility and high throughput capacity. Experimental data (13) on similar reaction systems in counter-current packed bed columns indicate increased column efficiency with increasing gas and liquid flows up to the point of flooding. For the present purposes, the cocurrent flow mode appeared more advantageous because of delayed flooding, reduced excess gas entrainment, and simplification of equipment, operational and analytical requirements.

DESIGN CONSIDERATIONS

Design criteria were based on expected process parameters for an integrated mini plant circuit with a solution flow rate of up to 1 L/min (4). The feed to chlorination (raffinate) would typically contain about 1 M $FeCl_2$, 3 M NaCl and 0.5 M HCl as major constituents. Preliminary calculations indicated that a standard column consisting of Corning 5 cm dia. beaded glass sections, packed to a height of 50 cm with 1 cm diameter glass Raschig rings, should be adequate for handling the specified solution flow.

Estimates of various fundamental parameters needed for the design of the column were obtained from the literature (9-14), and are summarized in Table 1.

The overall mass transfer equation for a gas-liquid reaction is, in standard notation (10) and units of $mol/m^3.s$:

$$-r_A''' = p_A/(1/k_{Ag}a + H_A/k_{Al}aE + H_A/kC_Bf_1) \quad (1)$$

Subscripts g or l refer to the gas and liquid phase, and A or B refer to the reactive species, respectively. With A = Cl_2, bB = $2Fe^{2+}$, and X = $2Fe^{3+} + 2Cl^-$, the overall reaction is:

$$A_{(g)} + bB_{(l)} \longrightarrow X_{(l)} \quad (2)$$

The molecular rate of chlorine transfer in a reactor segment of unit volume ($-r_A'''$) is primarily dependent on the type of packing, the gas and liquid flow rates, and the position of the volume element along the column. Estimates of the mass transfer coefficients k, k_{Ag} and k_{Al} were obtained as described below.

Crabtree and Schaefer (9) suggested that both Cl_3^- and Cl_2 are the primary reactive oxidants and derived the following expressions:

$$Cl_2 + Cl^- \underset{}{\overset{K}{\rightleftharpoons}} Cl_3^- \quad (3)$$

$$d[Fe^{3+}]/dt = 2k[Fe^{2+}][\Sigma Cl_2] = \quad (4)$$

$$2k'[Fe^{2+}][Cl_3^-] + 2k''[Fe^{2+}][Cl_2]$$

$$k = (k'K[Cl^-] + k'')/(1 + K[Cl^-]) \quad (5)$$

For the raffinate, $[Cl^-]$ = 5.5 mol/L, and the recommended values of K = 0.176 L/mol, k' = 910 L/mol.s and k'' = 163 L/mol.s yield the overall second order reaction rate constant, <u>k = 530 L/mol.s</u>.

Onda et al. (15) derived empirical relationships for the calculation of the mass transfer coefficients in the gas and liquid films at the interface. Conversion of their equations to SI units and insertion of the values listed in Table 1 for the specified column yielded:

$$k_g a = 0.0194\ G^{0.7}\ (mol/m^3.kPa.s) \tag{6}$$

$$k_l a = 0.0888\ L^{2/3}\ (s^{-1}) \tag{7}$$

As noted in Table 1, the volumetric gas and liquid flow rates are given in L (STP)/min. The three terms in the denominator of equation (1) are called the gas, liquid and chemical resistances, and their respective values at the expected column inlet and outlet conditions are listed in Table 2. At the inlet (bottom) of the column, the gas film resistance dominates since the reaction rate in fresh solution is very high, and this enhances the absorption of the gas into the liquid (E = 50, see reference 11). At the outlet or top of the column, both chemical and liquid film resistances have increased appreciably because the driving force (concentration potential) has decreased significantly (C_B = 0.001, E = 1). Since pure Cl_2 is used, however, the gas flow rate has decreased proportionally so that the gas film resistance has also increased. As a result, the complete process can be considered to be under gas film control, and this allows an analytical approximation to the solution of equation (8):

$$0.06 \times (-r_A'''')dV_R = dG/V_O = LdC_B/b \tag{8}$$

The 0.06 term converts r_A'''' from $mol/m^3.s$ to mol/L.min, yielding mol/min for the three expressions. The analytical approximation for gas film control is:

$$-r_A'''' = p_A k_{Ag} a = 0.0194\ p_A G^{0.7} \tag{9}$$

Integration of equation (8) then yields the following expression for the volume of the chlorination reactor:

$$V_R = (G_{in}^{0.3} - G_{out}^{0.3})/(0.0194p_A \times 0.06V_O \times 0.3) \quad (10)$$

Alternatively, the parameters of equation (1) can be evaluated at discrete intervals along the column. Changes in G and C_B are given by equation (8) for small steps in dV = dl x A. The iterative evaluation is continued until C_B attains the design criterion of Fe^{2+} <0.001 mol/L. Results of the two types of calculation are shown in Figure 1, and details of the mathematical methods used and listings of the appropriate computer programs may be obtained from the authors. For either calculation technique, a flow rate of up to 1 L/min requires a column length of about 50 cm. Figure 1 also shows that the agreement between the iterative and approximate solutions is good, and that the column efficiency continues to increase with higher liquid flow rates (tangents at high flow rates intercept the x axis at about 40 cm). Maintenance of constant flows and levels, however, will become increasingly difficult at higher flow rates, and the chances of flooding the column will increase. The purpose of the experimental part of this work was to investigate these limitations and to test whether the theoretical estimates were correct.

EXPERIMENTAL

The column reactor was assembled from 30 cm long sections of 5 cm diameter beaded glass tubes, joined by standard metal clamps to withstand pressures up to 500 kPa. The bottom inlet manifold consisted of a plastic plug, modified to hold a liquid inlet tube and a fritted gas diffuser tube. The column was packed with 1 cm diameter thin-walled glass Raschig rings

to a height of 50 cm above the gas diffuser. Solution was withdrawn via a T section above this packed bed, and an extra 30 cm section was provided above the T for gas/liquid disengagement and flexible level control purposes. The advantages over a countercurrent column are felt to be decreased turbulence, simplified liquid inlet (no distributor) and no special gas/liquid disengagement requirements. Several peripheral configurations were tested at relatively low flow rates, and Figure 2 shows the design considered to be most suitable for the higher flow rates.

Synthetic ferrous chloride solution was prepared by reduction of ferric chloride product solutions with iron powder and dilution to a suitable volume, thus building up a larger stock of solution after each test. The solution was pumped into an agitated precontactor to preoxidize the feed to the column and to scrub the gas exiting the column. The solution was then pumped into the bottom of the column in cocurrent flow with chlorine gas from a cylinder. Product solution overflowed into a small beaker for e.m.f. measurement, and thence into larger storage vessels. The exit gas from the column was very much diminished in volume, and the remainder was almost completely absorbed in the precontactor. Any remaining chlorine was absorbed into 1 L of 2 M NaOH solution.

For tests with different flow rates, different rotameters and peristaltic pump heads were used. Calibration curves for these accessories were determined by utilizing iodometric titration of the chlorine absorbed in NaOH. Samples were periodically withdrawn after the column and the precontactor, and iron was titrated against a standardized potassium dichromate solution. The weight loss of the Cl_2 cylinder after each prolonged run was also determined, and the scrubber solution was occasionally analyzed by the acidimetric and iodometric methods. Figure 3 compares the

analytical results for chlorine absorption by three different methods. Absorption in NaOH followed by iodometric titration of an aliquot is considered the most practical and reliable method.

RESULTS AND DISCUSSION

Preliminary runs at liquid flows of less than 250 mL/min and without a precontactor (Fig. 2) showed a very sharp transition between the pale green feed solution and the brown product solution at the gas inlet level, indicating a very rapid reaction and ideal plug flow conditions. The solution was heated slightly and the outlet e.m.f. was very sensitive to the gas:liquid flow ratio. High ferrous conversion efficiencies characterized by redox potentials greater than 500 mV SCE were achieved only with a large excess of Cl_2. At this point, it was decided that the precontactor should be included in the design and, henceforth, the test results improved.

A reliable mode of operation was to start with a washed and drained column and a prefilled precontactor. Solution and gas flows were then established at low rates to produce an outlet e.m.f. of about 550 mV SCE. This could be achieved for a wide range of conversion ratios between precontactor and column. The liquid and gas flows were then increased to higher rates while maintaining the same operational conditions and steady solution levels in all vessels. Readings and samples were taken during the periods of steady operation, and responses to flow rate changes were readily observed in a few minutes even at the lowest flow rates. The available flow control equipment limited operation to a maximum solution flow of only 800 mL/min and about 9 L/min of gas flow. Although steady state conditions were difficult to achieve at these high flow rates, no flooding was observed.

Details of three typical test runs are summarized in Table 3 which demonstrates the ranges explored in this study. An early run A showed that a single column must be operated with 80% excess Cl_2 to achieve up to 90% conversion. Better results were obtained in run B with the precontactor operated at 15 to 20% conversion, and at relatively low flow rates. Up to 97% ferrous conversion was achieved with 50% excess chlorine, and 90% conversion was realized with about 30% excess Cl_2. Run C confirmed these figures for higher flow rates, up to 800 mL/min, and a 5-10% conversion in the precontactor. The observation that most of the exit gas is absorbed in the precontactor, however, indicates that the bulk of the excess gas must be lost by leakage; e.g., through the silicone tubing used in the test. Titration of the scrubber solution suggests that only 10 to 15% excess Cl_2 is required to achieve 97% conversion.

At this point of the test program, up to 100 L of product solution was being regenerated in less than 2 h, and reagent and storage space requirements increased correspondingly. Since the feasibility of the design had been demonstrated for use in a mini plant circuit, the objectives of this study were considered to have been met. For practical reasons it was decided to conduct more accurate and detailed measurements in smaller, laboratory scale columns with more sophisticated pumping and control accessories. Work of this type, including measurements at higher pressures and temperatures, is currently in progress and will be reported separately.

CONCLUSIONS

This study has shown that preliminary calculations and reaction considerations are useful in the design of a mini plant scale continuous chlorination reactor. Tests indicate that design flow rates can be achieved with a surprisingly compact column if appropriate peripheral accessories are available. Theoretical estimates appear to be of the correct order of magnitude, but are a little too optimistic since a precontactor (additional stage) is required. More accurate measurements are required to test the validity of estimated parametric values for the purposes of scale-up engineering. Further tests should also be conducted to establish the effect of different temperatures, pressures, flow rates and ratios, concentrations, etc. on the efficiency of the process. These studies are more advantageously carried out in smaller laboratory scale columns prior to confirmation on a mini plant or pilot plant scale.

The present study has indicated that the continuous chlorination of the specified raffinate is relatively straightforward at room temperature. Since the reaction is exothermic and the solubility of Cl_2 decreases with temperature, higher temperatures may reduce the mass transfer rates and may cause precipitation of iron compounds, $CaSO_4$, NaCl and $PbCl_2$ because of evaporation, etc.

Other considerations (~~net Cl_2~~ production, Fe and SO_4 balances, energy balance) suggest that it might also be advantageous to carry out the low temperature chlorination directly after purification, followed by treatment of a bleedstream for iron rejection and impurity control, as indicated in Figure 4. Alternatively, part of the purified solution could be chlorinated and part subjected to air oxidation in a parallel circuit to oxidize some of the solution and to precipitate iron, gypsum, etc. (Fig. 5).

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Table 1. Parameters Used For Design Considerations

Symbol	Description	Value	Units
A	Cross sectional area of column	0.02	m^2
a	Specific packing surface area	550	m^2/m^3
b	Stoichiometric factor	2	-
C_B^{in}	Ferrous concentration, in	1	mol/L
C_B^{out}	Ferrous concentration, out	0.001	mol/L
D_{Ag}	Diffusion coefficient, Cl_2/Cl_2	1.13 E-6	m^2/s
D_{Al}	Diffusion coefficient, Cl_2/H_2O	1.44 E-9	m^2/s
d_s	Equivalent packing diameter	0.0134	m
E_{in}	Maximum absorption enhancement factor	50	-
ϵ	Void fraction	0.63	-
$f_{l,in}$	Liquid flow fraction, in	0.0744	-
G_{in}	Gas inflow rate, design	12.45	L/min
g	Gravity constant	0.81456	m/s^2
H_A	Henry's law constant	1.1	$kPa.m^3/mol$
k	Chlorination rate constant	530	L/mol.s
k_{Ag}^{in}	Maximum gas film mass transfer coefficient	0.113	$mol/m^3.kPa.s$
K_{Al}	Liquid film mass transfer coefficient	0.089	s^{-1}
L	Liquid flow rate, design	1.0	L/min
l	Length of column, actual	0.50	m
M_A	Chlorine molecular weight	70.9	g/mol
μ_g	Gas viscosity	0.01332	g/m.s
μ_l	Liquid viscosity	0.36617	g/m.s
p_A	Partial pressure, chlorine	150	kPa
R	Ideal gas constant	0.0082	$kPa.m^3/K.mol$

Symbol	Description	Value	Units
$-r''_{A,in}$	Mass transfer rate, maximum	16.5	$mol/m^3.s$
ρ_g	Gas density	3.22 E3	g/m^3
ρ_l	Liquid density	1.275 E6	g/m^3
T	Temperature, design	303	K
V_R	Reactor volume, calculated	0.91 to 0.99	L
V'_R	Reactor volume, actual	0.982	L
V_O	Ideal gas volume	22.414	L/mol

Table 2. Gas, Liquid and Chemical Resistances Under Anticipated Flow Conditions

Position	Resistances (m^3.kPa.s/mol)			Flows (L/min)		C_B
	R_g	R_l	R_{ch}	L	G	(mol/L)
Inlet (Bottom)	8.83	0.248	0.024	1.0	12.45	1.0
Outlet (Top)	44.3	0.619	0.506	1.0	1.25	0.001

Table 3. Experimental Results for Three Typical Runs

Run #	Inlet (L/min)		Column Outlet			°C	% Cl_2* Supplied
	L	G	% Conv.	pH	emf		
A. Single Stage	0.08	1.0	52.3	0.5	455	25	112
	0.08	1.2	79.1	0.45	494	30	134
	0.13	2.0	69.1	0.45	483	30	137
	0.11	2.2	88.0	0.3	514	30	178
B.† Double Stage	0.15	2.8	100.0	0.1	1075	34.7	179
	0.15	2.3	93.1	0.4	534	n.a.	147
	0.25	3.8	97.1	0.4	550	35.0	146
	0.25	3.4	87.3	0.3	507	35.5	130
C.†† Double Stage	0.40	5.0	97.1	0.1	550	n.a.	147
	0.40	5.0	97.1	0.1	560	40	147
	0.65	7.0	87.3	0.3	520	n.a.	127
	0.80	8.0	81.6	0.3	508	38	118

* Estimates based on flowmeter readings, pump calibration curves and initial ferrous ion concentration. High chlorine losses through leaks or diffusion through silicone rubber tubing are suspected.

† 15 to 20% conversion in the precontactor

†† 5 to 10% conversion in the precontactor

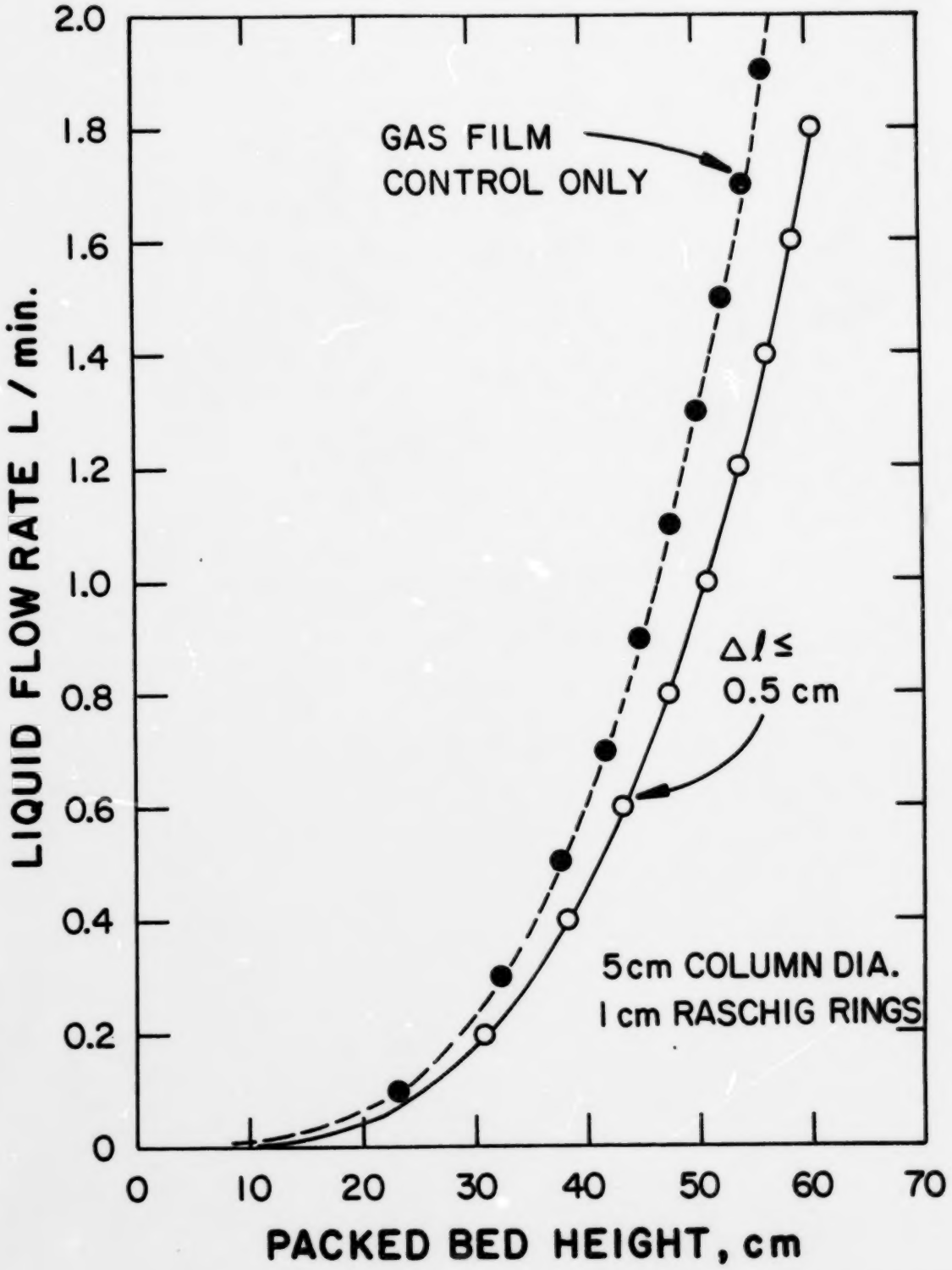
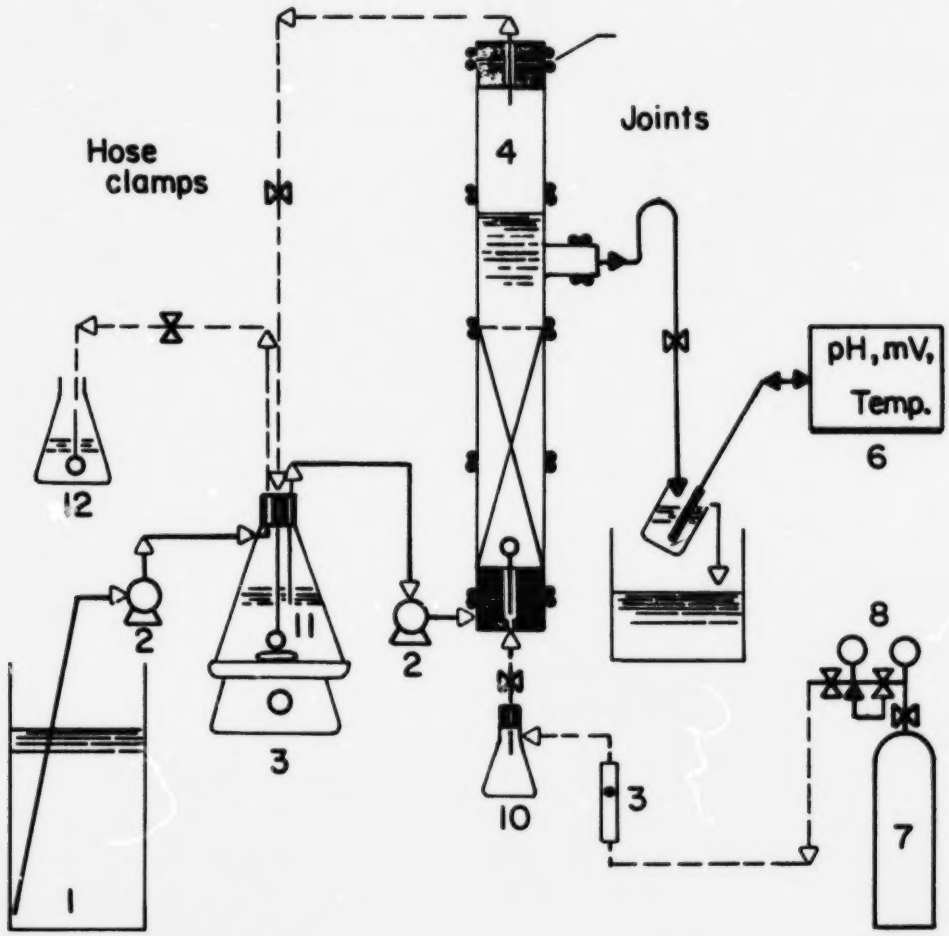


Figure 1. Theoretical Design Curves for the Chlorination of $FeCl_2$ Solutions in Packed Columns



——— Liquid:

1. Feed Tank
2. Masterflex Pumps
3. Precontactor
4. Column
5. Product Overflow
6. Meters

------ Gas:

7. Cylinder
8. Regulator
9. Flowmeter
10. Washbottle
11. Spargers
12. Scrubber

Figure 2. Experimental Set up

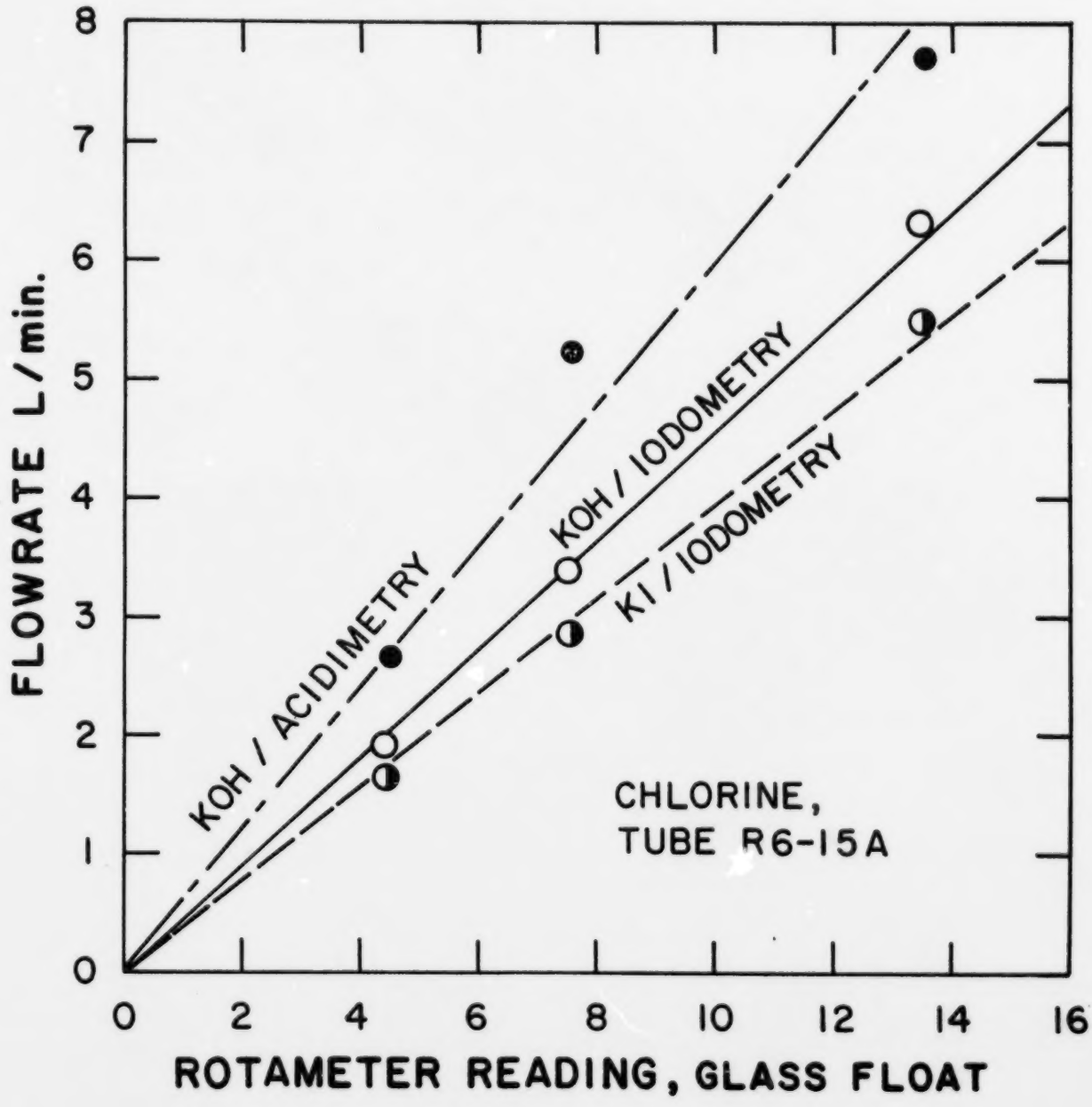
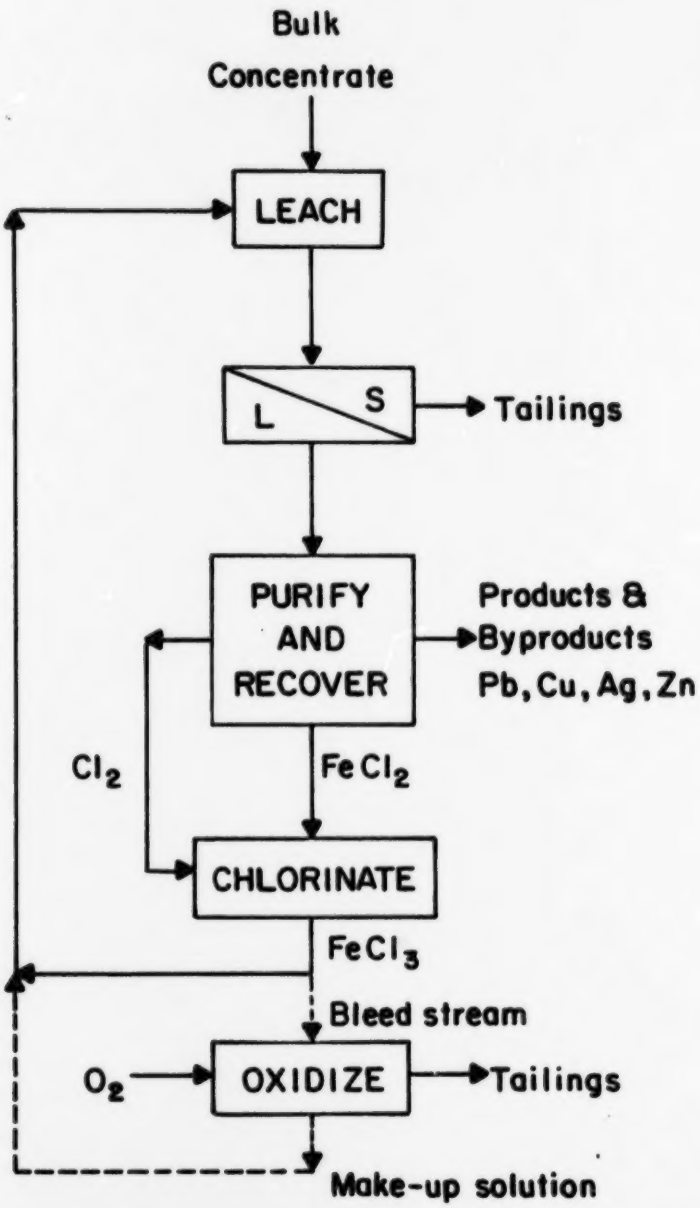


Figure 3. Comparison of Chlorine Calibration Methods



_____ Major Flows

--------- Minor Flows

Figure 4. Simplified Process Flow Sheet Illustrating the Chlorination of all the Process Solution

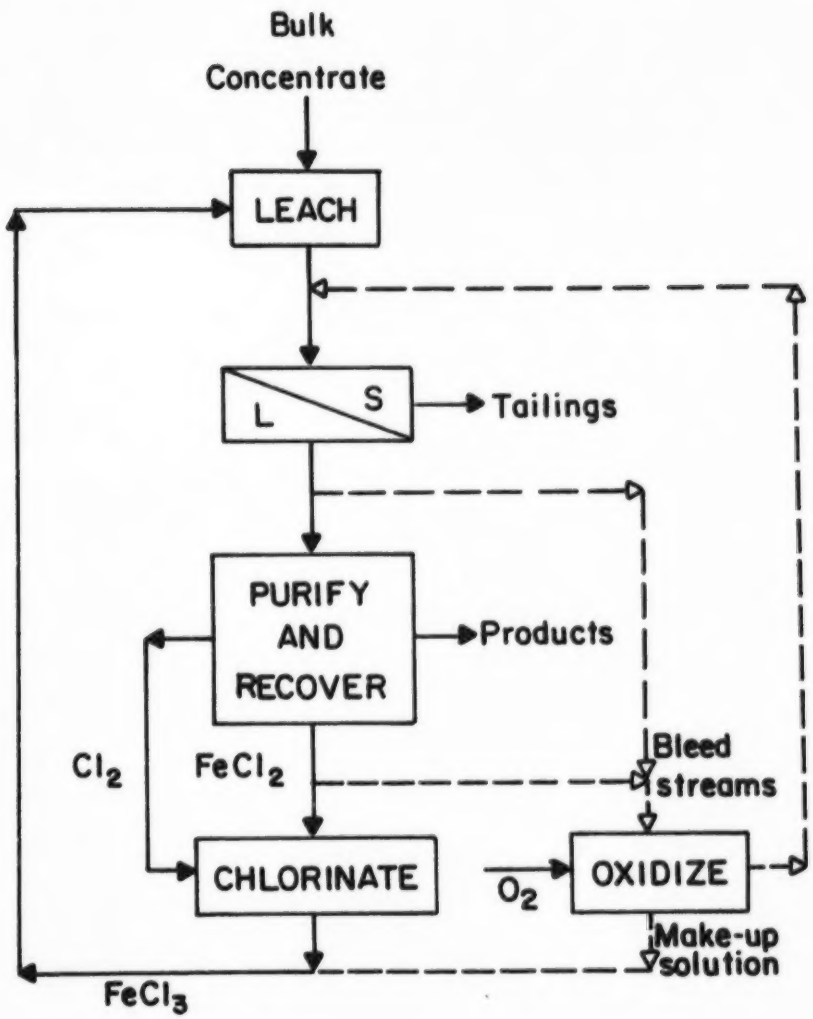


Figure 5. Alternative Process Option Showing the Chlorination of Part of the Process Solution